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(54) Title: DISHWASHING COMPOSITIONS COMPRISING A PHOSPHOLIPASE AND AN AMYLASE

(57) Abstract

The present invention relates to dishwashing compositions comprising a phospholipase and amylase for effective stain removal, especially greasy/oily, starchy and highly coloured stains and soils. The dishwashing compositions of the present invention also provide the prevention of the staining/discolouration of the dishware and plastic components of the dishwasher by highly coloured components and the avoidance of the formation of lime soap deposits on the dishware.

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DISHWASHING COMPOSITIONS COMPRISING A PHOSPHOLIPASE AND AN AMYLASE

Technical Field

The present invention relates to a dishwashing composition comprising a phospholipase enzyme and an amylase enzyme.

Background of the Invention

Performance of a detergent product is judged by a number of factors, including the ability to remove soils, and the ability to prevent the redeposition of the soils, or the breakdown products of the soils on the dishware in the wash. In particular, food soils are often difficult to remove effectively from a soiled item.

Food soils such as greasy/oily soils and stains represent a well-known cleaning challenge often met by the inclusion of a lipolytic enzyme in the detergent compositions. Lipolytic enzymes for enhanced removal of triglycerides containing soils and stains are indeed well-known in the art. Some examples are WO95/04808, WO93/21229 and WO94/25556. In addition to the lipolytic enzyme, a lime soap dispersant is generally also included in dishwashing

compositions to provide the mitigation of spotting and filming effects, particularly on glassware and plastic ware, such as described in WO95/04806, WO94/07985 and WO94/07984.

Processed or cooked food soils and stains often contain materials used for the processing, cooking and flavouring of the food : butter, milk, eggs, oils such as soya or olive oil, thickeners, sweeteners such as sugar. These materials are often based on proteins, fats and/or starches. In addition, such soils and stains are generally accompanied by amylose, sugars and their derivatives.

Highly coloured or 'dried-on' soils derived for example, from fruit and/or vegetables are also particularly challenging soils to remove. These coloured stains contain highly coloured compounds based on carotenoids compounds such as α-,β- and γ-carotene and lycopene and xanthophyls (zeaxanthin or capsanthin), or porphyrins such as chlorophyll and flavonoid pigments and dye components. This latter group of natural flavonoid based dye components comprises the highly coloured anthocyanins dyes and pigments based on pelargonidin, cyanidin, delphidin and their methyl esters and the antoxanthins. These compounds are the origin of most of the orange, red, violet and blue colours occurring in fruits and are abundant in all berries, cherry, red and black currents, grapefruits, passion fruit, oranges, lemons, apples, pears, pomegranate, red cabbage, red beets and also flowers. Carotenoids soils are derived from carrots and tomatoes and in any processed products containing these components as well as certain tropical fruits and saffron.

Furthermore these coloured food soils may be removed from soiled articles into the wash solution, and then may be redeposited from the wash solution onto other articles in the wash or onto the interior of the dishwashing machine. The problem is particularly noticeable when the wash load includes articles soiled by foods naturally containing significant levels of coloured dyestuff molecules, including for example tomato sauce and curry.

The Applicant has found that plastic articles in the wash, and especially areas of the interior of the dishwashing machine which are made of plastic material, are particularly susceptible to the staining/discolouration of the dishware by coloured

food soils. Said soils can interact with the surface of such plastic substrates producing staining which can be very difficult to remove.

A number of the Applicant's copending European Patent Applications have proposed solutions to solve the problem of coloured food dyestuff deposition in a machine dishwashing method. For example, EP 692 947 provides an efficient dye transfer inhibiting composition for use in a machine dishwashing method. The composition comprises an enzymatic system capable of generating hydrogen peroxide in combination with certain metallo catalysts. EP 740 521 describes the use of diacyl and tetraacyl peroxide bleaching species for inhibiting the transfer of bleachable food soils and enhancing their removal from plastic substrates.

Therefore, it is an object of the present invention to formulate dishwashing compositions providing effective stain removal, especially on greasy/oily, starchy and/or highly coloured stains and soils. It is a further object of the present invention to formulate dishwashing compositions preventing the staining / discolouration of the dishware by highly coloured components while avoiding lime soap deposits on the dishware.

The above objectives have been met by formulating dishwashing compositions comprising a phospholipase and an amylase.

Phospholipase enzymes are described in the art : J07177884 describes a preparation of enzymes comprising a phospholipase for cleaners and leather processing. GB 2 247 025 discloses an enzymatic dishwashing or rinsing composition comprising a phospholipase. In combination with proteolytic enzymes, said composition is said to be effective in removing egg yolk soil and consequently reducing spotting on glassware.

Amylases are commonly used ingredients of dishwashing compositions and are extensively described in the art.

However, the combined use of phospholipase and amylase for effective stains removal, especially greasy/oily, starchy and highly coloured stains and soils, for the prevention of the staining / discolouration of the dishware by highly coloured

components and avoidance of the formation of lime soap deposits on the dishware, has never been previously recognised.

Summary of the Invention

The present invention relates to dishwashing compositions comprising a phospholipase and an amylase for effective stain removal, especially greasy/oily, starchy and highly coloured stains and soils. The dishwashing compositions of the present invention also provide the prevention of the staining / discolouration of the dishware and plastic components of the dishwasher by highly coloured components and the avoidance of the formation of lime soap deposits on the dishware.

Detailed Description of the Invention

Phospholipase and amylase enzymes :

An essential element of the dishwashing compositions of the present invention is a phospholipase. It has been surprisingly found that the combined use of phospholipase and amylase improves tough food cleaning, especially of fat based, starch based and highly coloured soils and stains, reduces the level of staining of dishware, especially plastic dishware or internal machine part, by highly coloured components - carotenoids in particular - and prevents lime soap deposits on the dishware.

Without wishing to be bound by theory, it is believed that the combined action of the amylase enzyme for the removal of starch-based components present in the stains and soils and the enzymatic action of the phospholipase on specific fat components, provides substantive stain removal, especially on greasy/oily, starchy and highly coloured stains and soils.

Without wishing to be bound by theory, it is indeed believed that the greasy/oily stains/soils carry coloured compounds and are able to absorb onto dishware, especially plastic material and cause staining. It is thought that the

phospholipase enzyme cleaves the insoluble phospholipids into free fatty acids and soluble lysophospholipids which do not carry the coloured compounds and therefore prevents the staining / discolouration of the dishware and plastic components of the dishwasher and achieves significant though food cleaning.

Lipolytic enzymes can be included into dishwashing compositions. However, these enzymes while providing a greasy stains removal benefit, do not always provide spotting and filming prevention benefits due to the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. It has been surprisingly found that the addition of a combination of a phospholipase with an amylase does provide effective prevention of the staining / discolouration of dishware, in particular plastic items, by highly coloured components without causing lime soap deposits on the dishware. It is indeed believed that the phospholipase enzyme is more selective than any other known lipase and produces significantly less fatty acids, resulting in substantively less lime soap deposits.

Substrate material which is most prone to receipt of the transfer of bleachable food soils is plastic material, such as polypropylene, polyethylene, polystyrene (including alkyl butyl styrene) or PVC, being dishware or any internal machine part. Such plastic substrate material may interact with any highly coloured food soils on the substrate surface to produce persistent staining / discolouration of the substrate. This staining is particularly visible on translucent plastic material, as is commonly employed for food storage boxes and tubs.

Suitable phospholipases for the present invention are :

EC 3.1.1.32 Phospholipase A1
EC 3.1.1.4 Phospholipase A2
EC 3.1.1.5 Lysophospholipase
EC 3.1.4.3 Phospholipase C
EC 3.1.4.4 Phospholipase D

Preferred phospholipases for the detergent compositions of the present invention are the EC 3.1.1.4 Phospholipase A2 and EC 3.1.1.5 Lysophospholipase. Commercially available phospholipases are Lecitase® from Novo Nordisk A/S and Phospholipase A2 from Sigma.

The phospholipase are generally included in the compositions of the present invention at a level of from 0.0001% to 2%, preferably 0.01% to 1% pure enzyme by weight of total composition.

Preferred phospholipases for specific applications are of the alkaline type, i.e. enzymes having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a pH ranging from 7 to 12. More preferred phospholipases are enzymes having their maximum activity at a pH ranging from 7 to 12.

The second essential element of the dishwashing composition of the present invention is an amylase enzyme.

Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).
Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect

to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

Preferred amylase enzymes for the dishwashing compositions of the present invention are selected from :
(a) an α-amylase derived from *B. licheniformis* known as Termamyl®;
(b) an α-amylase variant comprising a C-terminal part of an α-amylase derived from *B. licheniformis* and a N-terminal part of an α-amylase derived from *B. amyloliquefaciens* or *from B. stearothermophilus*, wherein the Met amino acid residue at position 197 has been substituted preferably by a Leu, Thr, Ala, Gly, Ser, Ile or Asp amino acid residue, known as Duramyl® ; and/or
(c) a variant of an α-amylase described in WO95/10603 having a specific activity higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay, especially a variant with improved thermal properties, as described in WO96/23873.

Also suitable are the isoamylase enzymes (EC 3.2.1.68). These debranching enzymes hydrolyse 1,6-α-D-glucosidic branch linkages in glycogen, amylopectin and their β-limit dextrins.

The amylolytic enzymes are generally incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

Preferred amylases for specific applications are of the alkaline type, ie enzymes having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a pH ranging from 7 to 12. More preferred amylases are enzymes having their maximum activity at a pH ranging from 7 to 12.

The phospholipase and amylase enzymes will preferably be incorporated into the dishwashing compositions of the present invention at a pure enzyme weight ratio between 4500:1 and 1:5, more preferably between 50:1 and 1:1.

They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

Dishwashing Detergent Compositions

The dishwashing detergent composition may also contain various other components including surfactants, detergent builders, alkalinity sources, other bleaching agents, lime soap dispersants, organic polymeric compounds including polymeric dye transfer inhibiting agents, crystal growth inhibitors, heavy metal ion sequestrants, enzymes and enzyme stabilisers, corrosion inhibitors, suds suppressors, solvents, and hydrotropes.

Surfactant system

A highly preferred component of the compositions herein is a surfactant system comprising surfactant selected from anionic, cationic, nonionic ampholytic and zwitterionic surfactants and mixtures thereof. The surfactant system is typically present at a level of from 0.5% to 40% by weight, more preferably 1% to 30% by weight, most preferably from 1.5% to 20% by weight of the compositions.

In one preferred execution the surfactant system consists of low foaming nonionic surfactant, preferably selected from ethoxylated and/or propoxylated nonionic surfactants, more preferably selected from nonionic ethoxylated/propoxylated fatty alcohol surfactants.

In an alternative preferred execution the surfactant system comprises high foaming anionic surfactant, particularly alkyl ethoxysulfate surfactant, in combination with a suds suppressing system.

Anionic surfactant

Essentially any anionic surfactants useful for detersive purposes can be included in the compositions. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary alkyl sulfates, alkyl ethoxysulfates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_6-C_{18} alkyl sulfates which have been ethoxylated with from

about 0.5 to about 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_6-C_{18} alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Anionic carboxylate surfactants suitable for use herein include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Preferred alkyl ethoxy carboxylates for use herein include those with the formula $RO(CH_2CH_2O)_x\ CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C_{13} or less, and the average x is from about 3 to 10 when the average R is greater than C_{13}, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C_{12} to C_{18} alkyl group.

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula $RO\text{-}(CHR_1\text{-}CHR_2\text{-}O)\text{-}R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R_1 or R_2 is a succinic acid radical or hydroxysuccinic acid radical, and R_3 is selected from the group

consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Preferred soap surfactants are secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should preferably contain no ether linkages, no ester linkages and no hydroxyl groups. There should preferably be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 11-13 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the preferred secondary soap surfactants:

A. A highly preferred class of secondary soaps comprises the secondary carboxyl materials of the formula R^3 $CH(R^4)COOM$, wherein R^3 is $CH_3(CH_2)x$ and R^4 is $CH_3(CH_2)y$, wherein y can be O or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of (x + y) is 6-10, preferably 7-9, most preferably 8.

B. Another preferred class of secondary soaps comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R^5-R^6-COOM, wherein R^5 is C^7-C^{10}, preferably C^8-C^9, alkyl or alkenyl and R^6 is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note: R^5 can be in the ortho, meta or para position relative to the carboxyl on the ring.)C. Still another preferred class of secondary soaps comprises secondary carboxyl compounds of the formula $CH_3(CHR)_k$-$(CH_2)_m$-$(CHR)_n$-$CH(COOM)(CHR)_o$-$(CH2)_p$-$(CHR)_q$-CH_3, wherein each R is C_1-C_4 alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18. In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion.

Especially preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactant

Essentially any anionic surfactants useful for detersive purposes can be included in the compositions. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C_6-C_{18} fatty alcohols and C_6-C_{18} mixed ethoxylated/propoxylated fatty alcohols are preferred surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C_{10}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula:

$$R^6\ \overset{O}{\overset{\|}{C}}\ N(R^7)2$$

wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

A suitable example of an alkyl aphodicarboxylic acid for use herein is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful in the present invention include those compounds having the formula :

$$R^3(OR^4)_xN(R^5)_2 \rightarrow O$$

wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 18 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydyroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferable 1, ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{18} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Betaine surfactant

The betaines useful herein are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group or C_{10-16} acylamido alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl,m and R^2 is a C_1-C_5 hydrocarbyl group, preferably a C_1-C_3 alkylene group, more preferably a C_1-C_2 alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C_{12-14} acylamidopropylbetaine; C_{8-14} acylamidohexyldiethyl betaine; 4[C_{14-16} acylmethylamidodiethylammonio]-1-carboxybutane; C_{16-18} acylamidodimethylbetaine; C_{12-16} acylamidopentanediethyl-betaine; [C_{12-16} acylmethylamidodimethylbetaine. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Sultaine surfactant

The sultaines useful herein are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group, more preferably a C_{12}-C_{13} alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl, and R^2 is a C_1-C_6 hydrocarbyl group, preferably a C_1-C_3 alkylene or, preferably, hydroxyalkylene group.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions herein. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched.

Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Detergent Builder System

A highly preferred component of the compositions herein is a detergent builder system wherein said detergent builder system is preferably present at a level of from 0.5% to 80% by weight, more preferably from 1% to 60% by weight, most preferably from 2% to 40% weight of the compositions.

The detergent builder system is preferably water-soluble, and can, for example, contain builder compound selected from monomeric polycarboxylates or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, the alkali metal, ammonium or alkanonammonium salts of bicarbonates, borates, phosphates, and mixtures of any of the foregoing.

Suitable water-soluble monomeric or oligomeric carboxylate builders can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity/constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably of between 4 and 7.5.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance. Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid,

malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of the detergent compositions.

Specific examples of carbonate builder compound include the alkali metal carbonates, bicarbonates and sesquicarbonates.

Specific examples of phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid. Preferably, no phosphate builder compound is present.

The compositions may also include less water soluble builders although preferably their levels of incorporation are minimized. Examples of such less water soluble builders include the crystalline layered silicates, and the largely water insoluble sodium aluminosilicates.

Alkalinity

An alkalinity source is a preferred component of the compositions herein. A useful alkalinity source is provided by silicates which also provide china care properties to the detergent formulation. Suitable silicates include the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 and metasilicate are the most preferred silicates.

Silicates are preferably incorporated in the compositions of the invention at a level of from 1% to 50%, preferably from 5% to 40%, most preferably from 5% to 30% by weight.

Bleaching agents

The detergent compositions herein may include bleaching agents selected from chlorine bleaches, inorganic perhydrate salts, peroxyacid bleach precursors, organic peryoxacids and/or metal containing bleach catalyst.

There may be provided a means of delaying the release of oxygen bleach, which could include any diacyl and/or tetraacyl bleaching species, into the wash solution. Said means may be provided, for example by coating a granular bleach component with a hydrophobic coating, or by choice of physical form of the bleach which has a slow rate of dissolution by virtue, for example of its density or particle size.

Delayed release of the oxygen bleach into the wash solution can be advantageous in the prevention of tarnishing of silverware in washload, particularly when a component designed to protectively coat the silver in the wash is also included in the formulation. Such silver tarnish prevention technologies are disclosed in the Applicant's co-pending European Applications Nos. 9370004.4, 93870090.3, 93201918.5 and 93202095.1.

Chlorine bleaching agents

Chlorine bleaches include the alkali metal hypochlorites and chlorinated cyanuric acid salts. The use of chlorine bleaches in the composition of the invention is preferably minimized, and more preferably the compositions contain no chlorine bleach.

Inorganic perhydrate bleaching agents

The dishwashing compositions herein preferably include an inorganic perhydrate salt, normally in the form of the sodium salt preferably at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated

form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in detergent compositions in accordance with the invention, is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in coated form. The most preferred coating material comprises mixed salt of an alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is form 0.1 to 3, preferably n is from 0.15 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material is sodium silicate of SiO_2 : Na_2O ratio from 1.6 : 1 to 3.4 : 1, preferably 2.8 : 1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Magnesium silicate can also be included in the coating. Other suitable coating materials include the alkali and alkaline earth metal sulphates and carbonates.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of usefulness in the detergent compositions.

Peroxyacid bleach precursors

The dishwashing compositions herein also preferably include a peroxyacid bleach precursor (bleach activator), usually in combination with an inorganic perhydrate salt. Peroxyacid bleach precursors are normally incorporated at a level of from 1% to 20% by weight, more preferably from 1% to 10% by weight, most preferably from 1% to 7% by weight of the compositions.

The peroxyacid bleach precursors typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836988, 864798, 1147871 and 2143231 and imides such as are disclosed in GB-A-855735 & 1246338.

Particularly preferred bleach precursor compounds are the N,N,N^1,N^1 tetra acetylated compounds of formula $(CH_3CO)_2$-$(CH_2)_x$-$(CH_3CO)_2$ wherein x can be O or an integer between 1 & 6.

Examples include tetra acetyl methylene diamine (TAMD) in which x=1, tetra acetyl ethylene diamine (TAED) in which x=2 and tetraacetyl hexylene diamine (TAHD) in which x=6. These and analogous compounds are described in GB-A-907356. The most preferred peroxyacid bleach precursor is TAED.

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds described in EP-A-0170386.

Other peroxyacid bleach precursor compounds include sodium trimethyl hexanoyloxy benzene sulfonate and sodium acetoxy benzene sulfonate.

Organic peroxyacids

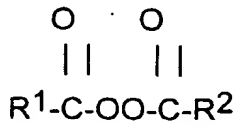
The dishwashing compositions may also contain organic peroxyacids at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

Useful organic peroxyacids include the amide substituted peroxyacids described in EP-A-0170386.

Other organic peroxyacids include diperoxy dodecanedioc acid, diperoxy tetra decanedioc acid, diperoxyhexadecanedioc acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

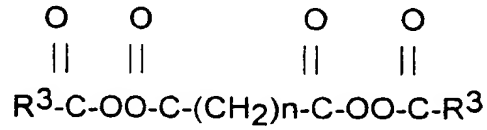
Diacyl and tetraacyl peroxide bleaching species

The diacyl peroxide bleaching species is preferably selected from diacyl peroxides of the general formula:



in which R^1 represents an aromatic group or a C_6-C_{18} alkyl, preferably C_6-C_{12} alkyl group containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents (e.g. $-N^+(CH_3)_3$,-COOH or -CN) and/or one or more interrupting moieties
(e.g. -CONH- or -CH=CH-) interpolated between adjacent carbon atoms of the alkyl radical, and R^2 represents an aliphatic or aromatic group compatible with a peroxide moiety, such that R^1 and R^2 together contain a total of 8 to 30 carbon atoms. Preferably R^1 and R^2 are linear unsubstituted C_6-C_{12} alkyl chains. Most preferably R^1 and R^2 are identical.

The tetraacyl peroxide bleaching species is preferably selected from tetraacyl peroxides of the general formula:



in which R^3 represents a C_1-C_9 alkyl, preferably C_3 - C_7, group and n represents an integer from 2 to 12, preferably 4 to 10 inclusive

Metal containing bleach catalyst

The compositions described herein may additionally contain as a preferred component, a metal containing bleach catalyst. Preferably the metal containing bleach catalyst is a transition metal containing bleach catalyst, more preferably a manganese or cobalt-containing bleach catalyst.

A suitable type of bleach catalyst is a catalyst comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Preferred examples include cobalt (III) catalysts having the formula:

$$Co[(NH_3)_nM'_mB'_bT'_tQ_qP_p]\ Y_y$$

wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and n + m + 2b + 3t + 4q + 5p = 6; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, nitrate, nitrite, sulfate, citrate, acetate, carbonate, and combinations thereof; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts (preferably less than about 0.2 volts) versus a normal hydrogen electrode.

Preferred cobalt catalysts of this type have the formula:

$$[Co(NH_3)_n(M')_m]\ Y_y$$

wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations

thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); m+n = 6; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[Co(NH_3)_5Cl]\ Y_y$, and especially $[Co(NH_3)_5Cl]Cl_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\ T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 $M^{-1}\ s^{-1}$ (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I_3^-, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^-, BF_4^-, $B(Ph)_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, etc. Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F^-, SO_4^{-2}, NCS^-, SCN^-, $S_2O_3^{-2}$, NH_3, PO_4^{3-}, and carboxylates (which preferably are mono-carboxylates, but more than one carboxylate may be present in the moiety as

long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, $HOC(O)CH_2C(O)O$-, etc.) Preferred M moieties are substituted and unsubstituted C_1-C_{30} carboxylic acids having the formulas:

$RC(O)O$-

wherein R is preferably selected from the group consisting of hydrogen and C_1-C_{30} (preferably C_1-C_{18}) unsubstituted and substituted alkyl, C_6-C_{30} (preferably C_6-C_{18}) unsubstituted and substituted aryl, and C_3-C_{30} (preferably C_5-C_{18}) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of $-NR'_3$, $-NR'_4^+$, $-C(O)OR'$, $-OR'$, $-C(O)NR'_2$, wherein R' is selected from the group consisting of hydrogen and C_1-C_6 moieties. Such substituted R therefore include the moieties $-(CH_2)_nOH$ and $-(CH_2)_nNR'_4^+$, wherein n is an integer from 1 to about 16, preferably from about 2 to about 10, and most preferably from about 2 to about 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched C_4-C_{12} alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as k_{OH}) for cobalt pentaamine catalysts complexed with oxalate (k_{OH}= 2.5 x 10^{-4} M^{-1} s^{-1} (25°C)), NCS^- (k_{OH}= 5.0 x 10^{-4} M^{-1} s^{-1} (25°C)), formate

(k_{OH}= 5.8 x 10^{-4} M^{-1} s^{-1} (25°C)), and acetate (k_{OH}= 9.6 x 10^{-4} M^{-1} s^{-1} (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]$ T_y, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article hereinbefore and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952); as well as the synthesis examples provided hereinafter.

These catalysts may be coprocessed with adjunct materials so as to reduce the color impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

Lime soap dispersant compound

The compositions herein may contain a lime soap dispersant compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap dispersant compound is preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. A numerical measure of the effectiveness of a lime soap dispersant is given by the lime soap dispersing power (LSDP) which is determined using the lime soap dispersion test as described in an article by H.C. Borghetty and C.A. Bergman, J.

Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to , for example, in the following review articles; W.N. Linfield, Surfactant Science Series, Volume 7, p3; W.N. Linfield, Tenside Surf. Det. , Volume 27, pages159-161, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm
$CaCO_3$ (Ca:Mg=3:2) equivalent hardness.

Polymeric lime soap dispersants suitable for use herein are described in the article by M.K. Nagarajan and W.F. Masler, to be found in Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). Examples of such polymeric lime soap dispersants include certain water-soluble salts of copolymers of acrylic acid, methacrylic acid or mixtures thereof, and an acrylamide or substituted acrylamide, where such polymers typically have a molecular weight of from 5,000 to 20,000.

Surfactants having good lime soap dispersant capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the invention include C_{16}-C_{18} dimethyl amine oxide, C_{12}-C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12}-C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of about 3 (LSDP=4), and the C_{13}-C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the trade names Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Organic polymeric compound

Organic polymeric compounds may be added to the dishwashing compositions herein. By organic polymeric compounds it is meant essentially any polymeric organic compounds commonly used as dispersants, anti-redeposition and soil suspension agents in detergent compositions.

Organic polymeric compound may be incorporated into the detergent compositions of the invention at a level of from 0.05% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Organic polymers containing acrylic acid or its salts having an average molecular weight of less than 15,000, hereinafter referred to as low molecular weight acrylic acid containing polymer, are particularly preferred organic polymeric compounds herein.

The low molecular weight acrylic acid containing polymers preferably have an average molecular weight of less than 15,000, preferably from 500 to 12,000, more preferably from 1,500 to 10,000, most preferably from 2,500 to 9,000.

The low molecular weight acrylic acid containing polymers may be either homopolymers or copolymers including the essential acrylic acid or acrylic acid salt monomer units. Copolymers may include essentially any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof.

Preferred commercially available low molecular weight acrylic acid containing homopolymers include those sold under the tradename Sokalan PA30, PA20, PA15 and PA10 by BASF GmbH, and those sold under the tradename Acusol 45N by Rohm and Haas.

Preferred low molecular weight acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula -[CR_2-CR_1(CO-O-R_3)]- wherein at least one of the substituents R_1, R_2 or R_3, preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen (i.e. a methyl acrylic acid monomer). The most preferred copolymer of this type

has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methyl acrylic acid.

Preferred commercially available low molecular weight acrylic acid containing copolymers include those sold under the tradename Sokalan CP10 by BASF GmbH.

Other suitable polyacrylate/modified polyacrylate copolymers include those copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents No.s 4,530,766, and 5,084,535 which have a molecular weight of less than 15,000.

Further examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are the copolymers of polyacrylate with maleic anhydride having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Other suitable organic polymeric compounds include the polymers of acrylamide and acrylate having a molecular weight of from 16,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 16,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

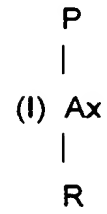
Polymeric dye transfer inhibiting agents

The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

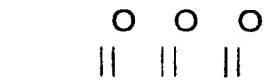
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



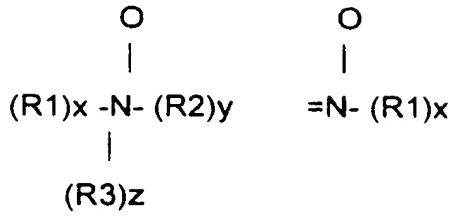
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to, or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



A is NC, CO, C, -O-,-S-, -N- ; x is O or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic,heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Preferred polymers for use herein may comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from

8,000 to 30,000, most preferably from 10,000 to 20,000. The preferred N-vinylimidazole N-vinylpyrrolidone copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The compositions herein may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

Polyvinylpyrrolidone may be incorporated in the compositions herein at a level of from 0.01% to 5% by weight of the detergent, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylpyrrolidone delivered in the wash solution is preferably from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

d) Polyvinyloxazolidone

The compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinyloxazolidone incorporated in the compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinyloxazolidone

delivered in the wash solution is typically from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

e) Polyvinylimidazole

The compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylimidazole incorpoarted in the compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylimidazole delivered in the wash solution is from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

Heavy metal ion sequestrants

Heavy metal ion sequestrants are useful components herein. By heavy metal ion sequestrants it is meant components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they bind heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are preferably present at a level of from 0.005% to 20%, more preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include the organo aminophosphonates, such as the amino alkylene poly (alkylene phosphonates)

and nitrilo trimethylene phosphonates. Preferred organo aminophosphonates are diethylene triamine penta (methylene phosphonate) and hexamethylene diamine tetra (methylene phosphonate).

Other suitable heavy metal ion sequestrants for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, or ethylenediamine disuccinic acid. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS), most preferably present in the form of its S,S isomer, which is preferred for its biodegradability profile.

Still other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EPA 317 542 and EPA 399 133.

In one preferred aspect of the invention any heavy metal ion sequestrant, particularly where said sequestrant comprises organo aminophosphonate components, is sprayed onto powdered sodium sulphate prior to incorporation into granular compostions in accord with the invention. This step leads to enhanced sequestrant stability in the granular detergent matrix.

Crystal growth inhibitor

A preferred component of the dishwashing compositions herein is a crystal growth inhibitor selected from organo diphosphonic acid or one of its salts/complexes. The organo diphosphonic acid component is preferably present at a level of from 0.005% to 20%, more preferably from 0.1% to 10%, most preferably from 0.2% to 5% by weight of the compositions.

The organo diphosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation and reference hereinafter to the acid implicitly includes reference to said salts or complexes. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

The organo diphosphonic acid is preferably a C_1-C_4 diphosphonic acid, more preferably a C_2 diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP).

Enzyme

Another optional ingredient useful in the dishwashing compositions herein is one or more enzymes. Preferred enzymatic materials include the commercially available lipases, neutral and alkaline proteases, esterases, cellulases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Other preferred enzymes that can be included in the compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677,

filed October 13, 1994. Variants of this "Protease D" include protease enzymes which are non-naturally-occurring carbonyl hydrolase variants having a different proteolytic activity, stability, substrate specificity, pH profile and/or performance characteristic as compared to the precursor carbonyl hydrolase from which the amino acid sequence of the variant is derived. As stated earlier, the protease enzymes are designed to have trypsin-like specificity and preferably also be bleach stable. The precursor carbonyl hydrolase may be a naturally-occurring carbonyl hydrolase or recombinant hydrolase. Specifically, such carbonyl hydrolase variants have an amino acid sequence not found in nature, which is derived by replacement of a plurality of amino acid residues of a precursor carbonyl hydrolase with different amino acids. The plurality of amino acid residues of the precursor enzyme correspond to position +210 in combination with one or more of the following residues: +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin.

The carbonyl hydrolase variants which are protease enzymes useful in the present invention compositions comprise replacement of amino acid residue +210 in combination with one or more additional modifications. While any combination of the above listed amino acid substitutions may be employed, the preferred variant protease enzymes useful for the present invention comprise the substitution, deletion or insertion of amino acid residues in the following combinations: 210/156; 210/166; 210/76; 210/103; 210/104; 210/217; 210/156/166; 210/156/217; 210/166/217; 210/76/156; 210/76/166; 210/76/217; 210/76/156/166; 210/76/156/217; 210/76/166/217; 210/76/103/156; 210/76/103/166; 210/76/103/217; 210/76/104/156; 210/76/104/166; 210/76/104/217; 210/76/103/104/156; 210/76/103/104/166; 210/76/103/104/217; 210/76/103/104/156/166; 210/76/103/104/156/217; 210/76/103/104/166/217 and/or 210/76/103/104/156/166/217; 210/76/103/104/166/222; 210/67/76/103/104/166/222; 210/67/76/103/104/166/218/222. Most preferably the variant enzymes useful for the present invention comprise the substitution, deletion or insertion of an amino acid residue in the following combination of residues: 210/156; 210/166; 210/217; 210/156/166; 210/156/217; 210/166/217;

210/76/156/166; 210/76/103/156/166 and 210/76/103/104/156/166 of *B. lentus* subtilisin with 210/76/103/104/156/166 being the most preferred.

Variant DNA sequences encoding such carbonyl hydrolase or subtilisin variants are derived from a precursor DNA sequence which encodes a naturally-occurring or recombinant precursor enzyme. The variant DNA sequences are derived by modifying the precursor DNA sequence to encode the substitution of one or more specific amino acid residues encoded by the precursor DNA sequence corresponding to positions +210, +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222 in *Bacillus lentus* or any combination thereof. Although the amino acid residues identified for modification herein are identified according to the numbering applicable to *B. amyloliquefaciens* (which has become the conventional method for identifying residue positions in all subtilisins), the preferred precursor DNA sequence useful for the present invention is the DNA sequence of *Bacillus lentus*. These recombinant DNA sequences encode carbonyl hydrolase variants having a novel amino acid sequence and, in general, at least one property which is substantially different from the same property of the enzyme encoded by the precursor carbonyl hydrolase DNA sequence. Such properties include proteolytic activity, substrate specificity, stability, altered pH profile and/or enhanced performance characteristics.

The protease enzymes useful herein encompass the substitution of any of the nineteen naturally occurring L-amino acids at the designated amino acid residue positions. Such substitutions can be made in any precursor subtilisin (procaryotic, eucaryotic, mammalian, etc.). Throughout this application reference is made to various amino acids by way of common one- and three-letter codes. Such codes are identified in Dale, M.W. (1989), Molecular Genetics of Bacteria, John Wiley & Sons, Ltd., Appendix B.

Preferably, the substitution to be made at each of the identified amino acid residue positions include but are not limited to substitutions at position +210 including I, V, L, and A, substitutions at positions +33, +62, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, and +218 of D or E, substitutions at position 76 including D, H, E, G, F, K, P and N; substitutions at position 103 including Q, T, D, E, Y, K, G, R and S; and substitutions at position 104 including S, Y, I, L, M, A, W, D, T, G and V; and substitutions at position 222 including S, C, A. The

specifically preferred amino acid(s) to be substituted at each such position are designated below in Table I. Although specific amino acids are shown in Table I, it should be understood that any amino acid may be substituted at the identified residues.

Table I

Amino Acid Residue	Preferred Amino Acid to be Substituted/Inserted
+210	I, V, L, A
+33, +62, +100, +101, +107 +128, +129, +130, +135 +156, +158, +164, +166 +167, +170, +209, +215 +217 and +218	D,E
+76	D,H
+103	A,Q,T,D,E,Y,K,G,R
+104	I,Y,S,L,A,T,G
+222	S, C, A

A comparison of the preferred amino acid residues identified herein for substitution versus the preferred substitution for each such position is provided in Table II.

Table II

	+210	+156	+166	+217	+76	+103	+104
B. amyloliquefaciens (wild-type)	P	E	G	Y	N	Q	Y
B. lentus (wild-type)	P	S	S	L	N	S	V
Most Preferred Substitution	I	E/D	E/D	E/D	D	A	I/Y

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption

and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the dishwashing compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.

Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Enzyme Stabilizing System

Enzyme-containing compositions herein may comprise from 0.001% to 10%, preferably from 0.005% to 8%,most preferably from 0.01% to 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, and mixtures thereof. Such stabilizing systems can also comprise reversible protease inhibitors.

The compositions herein may further comprise from 0% to 10%, preferably from 0.01% to 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from 0.5 ppm to 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during washing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely available, and are illustrated by salts containing ammonium cations or sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can be used if desired.

Corrosion inhibitor

The compositions may also contain corrosion inhibitor which is preferably incorporated at a level of from 0.05% to 10%, preferably from 0.1% to 5% by weight of the composition.

Suitable corrosion inhibitors include paraffin oil typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from 20 to 50; preferred paraffin oil selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68; a paraffin oil meeting these characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Other suitable corrosion inhibitor compounds include benzotriazole and any derivatives thereof, mercaptans and diols, especially mercaptans with 4 to 20 carbon atoms including lauryl mercaptan, thiophenol, thionapthol, thionalide and

thioanthranol. Also suitable are the C_{12}-C_{20} fatty acids, or their salts, especially aluminium tristearate. The C_{12}-C_{20} hydroxy fatty acids, or their salts, are also suitable. Phosphonated octa-decane and other anti-oxidants such as betahydroxytoluene (BHT) are also suitable.

Suds suppressing system

The compositions herein may comprise a suds suppressing system preferably present at a level of from 0.01% to 15%, more preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition. A suds suppressing system is a highly preferred component of the compositions when the surfactant system comprises high foaming surfactant.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl alcanol antifoam compounds, and paraffin antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon

atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight hydrocarbons such as paraffin, fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g., sodium, potassium, lithium) phosphates and phosphate esters. The hydrocarbons, such as paraffin and haloparaffin, can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms.

Copolymers of ethylene oxide and propylene oxide, particularly the mixed ethoxylated/propoxylated fatty alcohols with an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10, are also suitable antifoam compounds for use herein.

Suitable 2-alky-alcanols antifoam compounds for use herein have been described in DE 40 21 265. The 2-alkyl-alcanols suitable for use herein consist of a C_6 to C_{16} alkyl chain carrying a terminal hydroxy group, and said alkyl chain is substituted in the alpha position by a C_1 to C_{10} alkyl chain. Mixtures of 2-alkyl-alcanols can be used in the compositions according to the present invention.

Solvent

The compositions herein may contain organic solvents, particularly when formulated as liquids or gels. The compositions in accord with the invention preferably contain a solvent system present at levels of from 1% to 30% by weight, preferably from 3% to 25% by weight, more preferably form 5% to 20% by weight of the composition. The solvent system may be a mono, or mixed solvent system. Preferably, at least the major component of the solvent system is of low volatility.

Suitable organic solvent for use herein has the general formula $RO(CH_2C(Me)HO)_nH$, wherein R is an alkyl, alkenyl, or alkyl aryl group having from 1 to 8 carbon atoms, and n is an integer from 1 to 4. Preferably, R is an alkyl group containing 1 to 4 carbon atoms, and n is 1 or 2. Especially preferred R groups are n-butyl or isobutyl. Preferred solvents of this type are 1-n-butoxypropane-2-ol (n=1); and 1(2-n-butoxy-1-methylethoxy)propane-2-ol (n=2), and mixtures thereof.

Other solvents useful herein include the water soluble CARBITOL solvents or water-soluble CELLOSOLVE solvents. Water-soluble CARBITOL solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl; a preferred water-soluble carbitol is 2-(2-butoxyethoxy)ethanol also known as butyl carbitol. Water-soluble CELLOSOLVE solvents are compounds of the 2-alkoxyethoxy ethanol class, with 2-butoxyethoxyethanol being preferred.

Other suitable solvents are benzyl alcohol, and diols such as 2-ethyl-1,3-hexanediol and 2,2,4-trimethl-1,3-pentanediol.

The low molecular weight, water-soluble, liquid polyethylene glycols are also suitable solvents for use herein.

The alkane mono and diols, especially the C_1-C_6 alkane mono and diols are suitable for use herein. C_1-C_4 monohydric alcohols (eg: ethanol, propanol, isopropanol, butanol and mixtures thereof) are preferred, with ethanol particularly preferred. The C1-C4 dihydric alcohols, including propylene glycol, are also preferred.

Hydrotropes

Hydrotrope may be added to the compositions herein, and is typically present at levels of from 0.5% to 20%, preferably from 1% to 10%, by weight. Useful hydrotropes include sodium, potassium, and ammonium xylene sulfonates, sodium, potassium, and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions herein include perfumes, colours and fillers.

pH of the compositions

The automatic dishwashing compositions preferably have a pH as a 1% solution in distilled water at 20°C of from 8.5 to 13.0, preferably from 9.5 to 11.5, most preferably from 9.8 to 11.0. The manual dishwashing compositions preferably have a pH as a 1% solution in distilled water at 20°C of from 4 to 11.0, preferably from 5 to 8.

The pH of the compositions may be adjusted by the use of various pH adjusting agents. Preferred acidification agents include inorganic and organic acids including, for example, carboxylate acids, such as citric and succinic acids. Bicarbonates, particularly sodium bicarbonate, are useful pH adjusting agents herein. A highly preferred acidification acid is citric acid which has the advantage of providing builder capacity to the wash solution.

Form of the compositions

The dishwashing compositions herein can be formulated in any desirable form such as powders, tablets, granulates, pastes, liquids and gels.

Liquid compositions

The dishwashing compositions herein may be formulated as liquid compositions which typically comprise from 94% to 35% by weight, preferably

from 90% to 40% by weight, most preferably from 80% to 50% by weight of a liquid carrier, e.g., water, preferably a mixture of water and organic solvent.

Gel compositions

Gel compositions are typically formulated with polyakenyl polyether having a molecular weight of from about 750,000 to about 4,000,000.

Solid compositions

The dishwashing compositions herein may also be in the form of solids, such as powders, granules and tablets.

The particle size of the components of granular compositions should preferably be such that no more that 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The bulk density of granular detergent compositions is typically at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1100 g/litre.

Dishwashing method

The dishwashing method may be essentially any conventional dishwashing method.

The dishwashing method is preferably a machine dishwashing method performed using a dishwasher machine, which may be selected from any of those commonly available on the market. A machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. By an effective amount of detergent composition it is generally meant from 5g to 60g of detergent composition per wash, dissolved or dispersed in an aqueous wash solution volume of from 3 to 10 litres, to provide a wash solution concentration of the detergent composition of from 0.05% to 2% by weight. The wash temperature may be in the range 40°C to 65°C as commonly is employed in such methods. A rinse aid composition may also be used, if desired.

According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

Making processes - granular compositions

In general, granular detergent compositions can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

STPP	:	Sodium tripolyphosphate
Citrate	:	Tri-sodium citrate dihydrate
Bicarbonate	:	Sodium hydrogen carbonate
Carbonate	:	Anhydrous sodium carbonate
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 1.6-3.2)
Metasilicate	:	Sodium metasilicate (SiO_2:Na_2O ratio = 1.0)
PB1	:	Anhydrous sodium perborate monohydrate
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
Percarbonate	:	Anhydrous sodium percarbonate of nominal formula $2.Na_2CO_3.3H_2O_2$
Nonionic	:	C_{13}-C_{15} mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.

TAED	:	Tetraacetyl ethylene diamine
HEDP	:	Ethane 1-hydroxy-1,1-diphosphonic acid
DETPMP	:	Diethyltriamine penta (methylene) phosphonate, marketed by monsanto under the tradename Dequest 2060
MnTACN	:	Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
PAAC	:	Pentaamine acetate cobalt (III) salt
BzP	:	Benzoyl Peroxide
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
Protease	:	Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
Amylase	:	Amylolytic enzyme sold under the tradename Purafact Ox Am^R described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl®, Fungamyl® and Duramyl®, all available from Novo Nordisk A/S and those described in WO95/26397.
Lipase	:	Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
Phospholipase	:	Phosholipase enzyme sold under the tradename Lecitase® by Novo Nordisk A/S and/or Phospholipase A2 by Sigma.
BTA	:	Benzotriazole
PA30	:	Polyacrylic acid of average molecular weight approximately 4,500
MA/AA	:	Randon copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000
480N	:	Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500
Polygel/Carbopol	:	High molecular weight crosslinked polyacrylates.
Sulphate	:	Anhydrous sodium sulphate.
NaOCl	:	Sodium hypochlorite

NaDCC	:	Sodium dichloroisocyanurate
NaOH	:	Sodium Hydroxide solution
KOH	:	Potassium Hydroxide solution
NaBz	:	Sodium Benzoate
SCS	:	Sodium Cumene Sulphonate
pH	:	Measured as a 1% solution in distilled water at 20°C

Example 1

The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared in accord with the present invention:

	I	II	III	IV	V	VI	VII	VIII
STPP	-	-	54.3	51.4	51.4	-	-	50.9
Citrate	35.0	17.0	-	-	-	46.1	40.2	-
Carbonate	-	17.5	14.0	14.0	14.0	-	8.0	32.1
Bicarbonate	-	-	-	-	-	25.4	-	-
Silicate	32.0	14.8	14.8	10.0	10.0	1.0	25.0	3.1
Metasilicate	-	2.5	-	9.0	9.0	-	-	-
PB1	1.9	9.7	7.8	7.8	7.8	-	-	-
PB4	8.6	-	-	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7	11.8	4.8
Nonionic	1.5	2.0	1.5	1.7	1.5	2.6	1.9	5.3

	I	II	III	IV	V	VI	VII	VIII
TAED	5.2	2.4	-	-	-	2.2	-	1.4
HEDP	-	1.0	-	-	-	-	-	-
DETPMP	-	0.6	-	-	-	-	-	-
MnTACN	-	-	-	-	-	-	0.008	-
PAAC	-	-	0.008	0.01	0.007	-	-	-
BzP	-	-	-	-	1.4	-	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.6	-	-
Phosopholipase	0.01	0.05	0.5	0.5	1.0	0.5	0.05	0.5
Protease	0.072	0.072	0.029	0.053	0.046	0.026	0.059	0.06

Amylase	0.012	0.012	0.006	0.012	0.013	0.009	0.017	0.03
Lipase	-	0.001	-	0.005	-	-	-	-
BTA	0.3	0.3	0.3	0.3	0.3	-	0.3	0.3
MA/AA	-	-	-	-	-	-	4.2	-
480N	3.3	6.0	-	-	-	-	-	0.9
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1
Sulphate	7.0	20.0	5.0	2.2	0.8	12.0	4.6	-
pH	10.8	11.0	10.8	11.3	11.3	9.6	10.8	10.9
Miscellaneous and water				Up to 100%				

Example 2

The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared in accord with the present invention :

	I	II	III	IV	V	VI	VII	VII
STPP	30.0	30.0	33.0	34.2	29.6	31.1	26.6	17.6
Carbonate	30.5	30.5	31.0	30.0	23.0	39.4	4.2	45.0
Silicate	7.4	7.4	7.5	7.2	13.3	3.4	43.7	12.4
Metasilicate	-	-	4.5	5.1	-	-	-	-
Percarbonate	-	-	-	-	-	4.0	-	-
PB1	4.4	4.2	4.5	4.5	-	-	-	-
NADCC	-	-	-	-	2.0	-	1.6	1.0
Nonionic	1.2	1.0	0.7	0.8	1.9	0.7	0.6	0.3

	I	II	III	IV	V	VI	VII	VII
TAED	1.0	-	-	-	-	0.8-	-	-
PAAC	-	0.004	0.004	0.004	-	-	-	-
BzP	-	-	-	1.4	-	-	-	-
Paraffin	0.2	0.3	0.2	0.3	-	-	-	-
Phospholipase	1.0	1.05	0.5	1.0	0.5	0.1	0.5	1.0
Lipase	0.005	-	0.001	-	-	-	-	-
Protease	0.036	0.015	0.03	0.028	-	0.03	-	-
Amylase	0.003	0.003	0.01	0.006	0.02	0.01	0.015	0.015

BTA	0.1	0.1	0.1	0.1	-	-	-	-
Perfume	0.2	0.2	0.2	0.2	0.1	0.2	0.2	-
Sulphate	23.4	25.0	22.0	18.5	30.1	19.3	23.1	23.6
pH	10.8	10.8	11.3	11.3	10.7	11.5	12.7	10.9
Miscellaneous and water					Up to 100%			

Example 3

The following detergent composition tablets were prepared in accord with the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm^2 using a standard 12 head rotary press:

	I	II	III	IV	V	VI
STPP	-	48.8	49.2	38.0	-	46.8
Citrate	26.4	-	-	-	31.1	-
Carbonate	-	5.0	14.0	15.4	14.4	23.0
Silicate	26.4	14.8	15.0	12.6	17.7	2.4
Phospholipase	0.5	0.7	0.5	0.7	0.005	0.5
Protease	0.058	0.072	0.041	0.033	0.052	0.013
Amylase	0.01	0.03	0.012	0.007	0.016	0.002
Lipase	0.005	-	-	-	-	-
PB1	1.6	7.7	12.2	10.6	15.7	-
PB4	6.9	-	-	-	-	14.4
Nonionic	1.5	2.0	1.5	1.6	0.8	6.3
PAAC	-	-	0.02	0.009	-	-

	I	II	III	IV	V	VI
MnTACN	-	-	-	-	0.007	-
TAED	4.3	2.5	-	-	1.3	1.8
HEDP	0.7	-	-	0.7	-	0.4
DETPMP	0.6	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.5	-	-
BTA	0.2	0.3	0.3	0.3	-	-
PA30	3.2	-	-	-	-	-

MA/AA	-	-	-	-	4.5	0.5
Perfume	-	-	0.05	0.05	0.2	0.2
Sulphate	24.0	13.0	2.3	-	10.7	3.4
Weight of tablet	25g	25g	20g	30g	18g	20g
pH	10.6	10.6	10.7	10.7	10.9	11.2
Miscellaneous and water			Up to 100%			

Example 4

The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared in accord with the present invention :

	I	II	III	IV
STPP	17.5	17.5	17.2	16.0
Carbonate	2.0	-	2.4	-
Silicate	5.3	6.1	14.6	15.7
NaOCl	1.1	1.1	1.1	1.2
Polygen/carbopol	1.1	1.0	1.1	1.2
Nonionic	-	-	0.1	-
NaBz	0.7	0.8	-	-
Phospholipase	0.005	0.1	0.05	0.05
Amylase	0.01	0.005	0.0025	0.05
NaOH	-	1.9	-	3.5
KOH	2.8	3.5	3.0	-
pH	11.0	11.7	10.9	11.0
Sulphate, miscellaneous and water		up to 100%		

Example 5

The following liquid rinse aid compositions were prepared in accord with the present invention :

	I	II	III
Nonionic	12.0	-	14.5
Nonionic blend	-	64.0	-
Citric	3.2	-	6.5

HEDP	0.5	-	-
PEG	-	5.0	-
SCS	4.8	-	7.0
Phospholipase	0.05	0.1	1.0
Amylase	0.005	0.003	0.01
Ethanol	6.0	8.0	-
pH of the liquid	2.0	7.5	/

Example 6

The following liquid manual dishwashing detergent compositions were prepared in accord with the present invention :

	I	II	III	IV	V
Alkyl (1-7) ethoxy sulfate	28.5	27.4	19.2	34.1	34.1
Amine oxide	2.6	5.0	2.0	3.0	3.0
C12 glucose amide	-	-	6.0	-	-
Betaine	0.9	-	-	2.0	2.0
Xylene sulfonate	2.0	4.0	-	2.0	-
Neodol C11E9	-	-	5.0	-	-
Polyhydroxy fatty acid amide	-	-	-	6.5	6.5
Sodium diethylene penta acetate (40%)	-	-	0.03	-	-
Diethylenetriamine penta acetate	-	-	-	0.06	0.06
Sucrose	-	-	-	1.5	1.5
Ethanol	4.0	5.5	5.5	9.1	9.1
Alkyl diphenyl oxide disulfonate	-	-	-	-	2.3
	I	II	III	IV	V
Calcium formate	-	-	-	0.5	1.1
Ammonium citrate	0.06	0.1	-	-	-
Sodium chloride	-	1.0	-	-	-
Magnesium chloride	3.3	-	0.7	-	-
Calcium chloride	-	-	0.4	-	-

Sodium sulfate	-	-	0.06	-	-
Magnesium sulfate	0.08	-	-	-	-
Magnesium hydroxide	-	-	-	2.2	2.2
Sodium hydroxide	-	-	-	1.1	1.1
Hydrogen peroxide	200ppm	0.16	0.006	-	-
Phospholipase	0.01	0.05	0.5	1.0	0.005
Amylase	0.03	0.005	0.01	0.005	0.015
Protease	0.5	0.15	0.10	0.08	0.05
Perfume	0.18	0.09	0.09	0.2	0.2
Water and minors	Up to 100%				

CLAIMS

1. A dishwashing composition comprising a phospholipase and an amylase.

2. A dishwashing composition according to claim 1 wherein said phospholipase is selected from a phospholipase A2 and/or a lysophospholipase.

3. A dishwashing composition according to claims 1 to 2 wherein said amylase is selected from :
   (a) an α-amylase derived from *B. licheniformis*;
   (b) an α-amylase variant comprising a C-terminal part of an α-amylase derived from *B. licheniformis* and a N-terminal part of an α-amylase derived from *B. amyloliquefaciens* or *from B. stearothermophilus*, wherein the Met amino acid residue at position 197 has been substituted preferably by a Leu, Thr, Ala, Gly, Ser, Ile or Asp amino acid residue;
   (c) a variant as described in WO96/23873, of an α-amylase having a specific activity higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas ® α-amylase activity assay, especially a variant with improved thermal properties;
   and mixtures thereof.

4. A dishwashing composition according to claims 1 and 2 wherein said amylase is an isoamylase.

5. A dishwashing composition according to claims 1 to 4 wherein said phospholipase is comprised at a level of from 0.0001% to 2%, preferably from 0.01% to 1% pure enzyme by weight of total composition.

6. A dishwashing composition according to claims 1 to 5 wherein said amylase is comprised at a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of total composition.

7. A dishwashing composition according to any of the preceding claims wherein said phospholipase and amylase are present in a pure enzyme weight ratio between 4500:1 and 1:5, preferably between 50:1 and 1:1.

8. The use of a dishwashing composition according to any of the preceding claims for hand or machine dishwashing.

9. The use of a phospholipase and an amylase in a dishwashing composition, to provide effective stain removal, preferably greasy/oily, starch-based and highly coloured soils and stains removal.

10. The use of a phospholipase and an amylase in a dishwashing composition, to inhibit the transfer of a highly coloured food soil and/or stain from an aqueous wash solution to a substrate in a dishwashing method, with reduced formation of lime soap deposit.

11. The use according to Claim 10 wherein said highly coloured food soil and/or stain is of carotenoid nature.

12. The use according to Claims 10 to 11 wherein said substrate comprises plastic material.

INTERNATIONAL SEARCH REPORT

[redacted]ional Application No
[redacted]US 97/11399

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D C12N

Documentation searched other than minimumdocumentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 97 43376 A (THE PROCTER & GAMBLE CO.) 20 November 1997 see page 6, line 5 - line 35 see page 24, line 20 - page 27, line 13 see page 45, line 18 - line 31 see claims 1,2,10,11,13	1,8
A	GB 2 247 025 A (UNILEVER PLC.) 19 February 1992 cited in the application see the whole document	1,2,8
A	WO 96 23873 A (NOVO NORDISK A/S) 8 August 1996 cited in the application see page 36, line 21 - page 58, line 4 see claims 1-26	1,3

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publicationdate of another citation or other special reason (as specified)

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Date of the actual completion of theinternational search	Date of mailing of the international search report
4 March 1998	25/03/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A

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INTERNATIONAL SEARCH REPORT

International Application No
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